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(54) Polyurethane compositions containing a polyhydroxyalkylphosphine oxide.

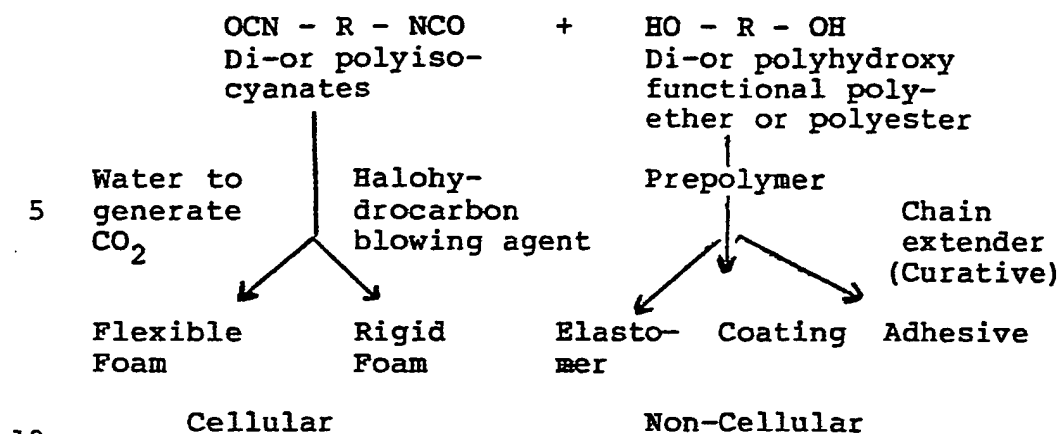
(57) This invention includes polyurethane elastomer products formed by curing a mixture of an NCO terminated methane prepolymer and a polyhydroxyalkylphosphine oxide, a curable polyurethane composition, which gives improved adhesives on curing, comprising an NCO urethane prepolymer and, as the curative therefor, a mixture of an aliphatic hydroxy compound and a polyhydroxyalkylphosphine oxide, and a heat curable polyurethane composition comprising a blocked NCO prepolymer and a hydroxyl curative containing a polyhydroxyalkylphosphine oxide.

POLYURETHANE COMPOSITIONS CONTAINING A POLYHYDROXYALKYL-  
PHOSPHINE OXIDE

This invention relates to polyurethanes, particularly to improved polyurethane compositions and their  
5 preparation for use as coatings, elastomers and adhesives.

Polyurethanes comprise a well-known class of commercial polymers, the characteristic structural unit of which is the urethane linkage,  $-\overset{\text{H}}{\text{N}}-\text{C}(\text{O})\text{O}-$ . Broadly, such polymers are produced by condensing a polyisocyanate  
10 with a multifunctional hydrogen donor such as an organic polyol, commonly a polyester or polyether having free hydroxy groups. Both cellular and solid forms of the polymer can be obtained, depending on the choice of reaction conditions. To produce cellular or, what is more  
15 familiarly referred to as polyurethane foam, the so-called "one shot" process is normally employed. In this procedure, all of the ingredients are combined simultaneously in the presence of a blowing agent and the resultant mixture transferred to a mold or form and allowed to foam up and solidify. Flexible foams are obtained by including as one of the components, a small  
20 quantity of water which hydrolyzes some of the isocyanate to generate carbon dioxide which acts as the blowing agent; rigid foams are produced using halogenated hydrocarbons as the blowing agent. Non-cellular polyurethanes are normally made without a blowing agent. In the "prepolymer" or two-component method of manufacturing non-cellular polyurethanes, the technique with  
25 which the invention is generally concerned, an excess of polyisocyanate is first reacted with the polyol to form an intermediate prepolymer. The latter is then contacted with an active hydrogen compound - commonly referred to as a curative - which reacts with residual NCO groups to engender a solid polyurethane system. Amines and hydroxy compounds are the usual curatives. An outline of  
30 polyurethane chemistry is set forth in the following scheme:

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By varying R, for example, aliphatic or aromatic, the molecular and/or equivalent weight of the reactants, functionality of active hydrogen donors, for example, polyols and curatives as well as the nature of other minor though important ingredients such as catalysts, surfactants and the like, a large variety of products having widely differing properties can be realized.

One important line of polyurethane products is known as elastomers. These are substantially linear polyurethanes having varying degrees of rubberlike properties. They are usually formed by reacting excess diisocyanate with linear long-chain polyols, such as a polyether or polyester, and curing the resulting NCO terminated prepolymer with a low molecular weight diamine, diol, triol or their admixtures.

In the manufacture of polyurethane elastomers made by the prepolymer or two-component method, one of the standard curatives for toluene diisocyanate (TDI) based prepolymers is MOCA, the acronym for the name of the difunctional amine 4,4'-methylene-bis(2-chloroaniline). However, because of possible carcinogenicity, the production and availability of MOCA has been considerably curtailed. Other amine curatives have been used such as Polacure 740M (trimethylene glycol di-p-amino benzoate).

It is also known to produce polyurethane elastomers using low molecular weight polyhydroxy compounds

as curatives. An example of such curatives, particularly for commercial purposes, is a blend, by weight, of 6% trimethylolpropane (TMP) and 94% 1,4-butanediol (BD). Although generally satisfactory as a curative for MDI based prepolymers, (TMP) (BD) gives soft, very low strength elastomers with TDI prepolymers compared to corresponding MOCA cured polymers. Other curatives which have been reported include mixtures of 1,4-butanediol and butynediol for RIM injection molded polyurethane elastomers and hydroquinone di-(beta hydroxyethyl) ether (HQEE) for sheet molded polyurethane elastomers (SMUC).

Curable adhesives are another valuable class of products which have been developed based on polyurethane resin technology. A curable polyurethane adhesive with which the present invention is particularly concerned, consists of a separate two-component system, one of which contains an NCO terminated prepolymer and the other of which is a low molecular weight aliphatic dihydroxy curative compound, 1,4-butanediol being commonly used. A trihydroxy compound, such as trimethylolpropane (TMP), may also be included as a modifier but the quantity is normally rather small, lest excessive cross-linking occur.

A further valuable and important use of polyurethanes is in the manufacture of coatings. Although numerous formulations have been developed over the years, polyurethane coatings normally fall within the five general types which have been classified by the American Society for Testing Materials (ASTM). Except for ASTM Type I, all are derived by curing a reactive precursor material in the form of an NCO terminated prepolymer. The latter is formed by condensing an excess of a polyisocyanate with an organic polyol, commonly a polyester or polyether having free hydroxy groups; curing of the NCO terminated prepolymer is effected by reacting it with a hydrogen donor, for

example, moisture, polyhydroxy compound or amine to give the final polymer product. ASTM Type II is a one-package moisture curable urethane prepolymer having a free NCO content of around 3 to 4%, at a non-volatile level of about 40 to 50%. The remaining isocyanate reacts with atmospheric moisture after it has been applied to give a film containing a large percentage of urea groups. ASTM Type III is a prepolymer having a high level of NCO which is tied up with a phenol to prevent subsequent reaction at ambient temperature. This type of material is known as a blocked urethane and is extensively used in coatings which are baked after application. The phenol splits off at temperatures in excess of about 350°F, after which curing of the coating proceeds very rapidly owing to the vigorous reaction between the available NCO and the hydrogen donor which could not occur as long as the NCO was combined with the phenolic blocking agent. ASTM Type IV is a two-package urethane, one of which contains the NCO prepolymer, the other of which contains a highly reactive diamine plus other ingredients to promote flow, bubble release and other minor components. ASTM Type V is also a two-package formulation where the first component is the NCO prepolymer and the second component is a polyol.

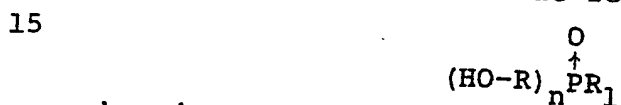
Of the ASTM classified urethane, Type III is emerging as the most important in the coating field. It is a single-package, prepolymer system which provides many of the advantages of two-component urethanes while devoid of the mixing and proportioning problems associated with two-component materials. Blocked urethanes are moisture insensitive, stable over long periods, and generally easy to transport, use and handle, requiring only that they be protected from undue heat.

Although coatings must exhibit various chemical and physical properties, for example, resistance to

marring, cracking, solvent attack, moisture penetration, discoloration, corrosion, U.V. breakdown; strength and hardness are also important. However, good adhesion to a substrate is perhaps the most  
 5 fundamental requisite.

In accordance with the present invention, polyurethane compositions have been developed embracing new classes of elastomers, adhesives and coatings which exhibit excellent chemical and physical properties.

10 The polyurethane elastomers of the invention can be produced by curing an NCO terminated prepolymer derived from a polyhydroxy polyether or polyester or mixtures in which the curative contains a polyhydroxy alkylphosphine oxide of the formula:



wherein R is alkylene of 3 to 6 carbon atoms,  $\text{R}_1$  is an alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 or 3.

20 In general, polyurethane elastomers of the invention are prepared generally in the known manner except that the herein polyhydroxyalkylphosphine oxides are used in place of the prior art curatives. Typically, the NCO prepolymer and the curative are each degassed,  
 25 mixed together and cured at about 80°C; post curing is usually at about 100°C.

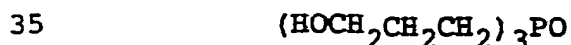
The prepolymers employed in the practice of the invention are known chemical entities, the description and preparation of which are extensively documented in  
 30 treatises dealing with urethane elastomer technology. Such intermediates are obtained by condensing an excess of an organic diisocyanate or polyisocyanate with various polyhydroxy-containing polyesters and polyethers. The percentage of NCO available in the resulting isocyanate terminated prepolymer will vary with the amount  
 35 of excess isocyanate employed. Solvent-free prepolymers are commonly made up at an available NCO percent-

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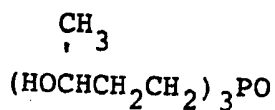
tage of about 3% to 20%. In the well-known treatise "The Development and Use of Polyurethane Products" by E. N. Doyle (McGraw-Hill Book Company) at page 35, the characteristics of some prepolymers derived from polyfunctional polyethers and polyesters in which the diisocyanate is TDI are as follows:

1. TDI/polyester, with 2.5 equivalent weight excess TDI, with the polyester having an equivalent weight of 810 (lightly branched polyethylene succinate).
2. TDI/polyether, with 2.5 excess TDI, with the polyether having an equivalent weight of 325 (polyether diol).
3. TDI/polyether, with 2.5 TDI, with the polyether having an equivalent weight of 980 (polyoxypropylene triol).
4. TDI/polybutadiene homopolymer, with 3.0 excess TDI. The equivalent weight of the homopolymer is 1,150.
5. TDI plus 0.75 equivalent weight of polyester with equivalent weight of 280, plus 0.25 equivalent weight polyether, with an equivalent weight of 960. 3.0 excess TDI was used. The polyester was propylene fumarate and the polyether a diol.
6. TDI plus 0.75 equivalent weight of polyoxypropylene glycol triol, with an equivalent weight of 1,000, plus 0.25 equivalent weight hydroxy ethyl acrylate. 2.5 excess TDI was used. The hydroxy ethyl acrylate had an equivalent weight of 116.
7. TDI plus 0.75 equivalent weight of polyoxypropylene glycol (same as in No. 6) plus 0.25 equivalent weight sorbitol. Excess TDI was 3.0.

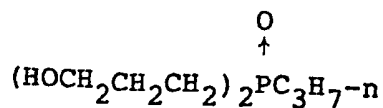
Exemplary phosphine oxides within the ambit of the formula aforesaid include:



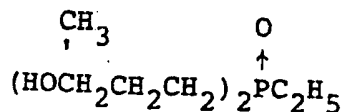
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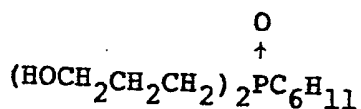
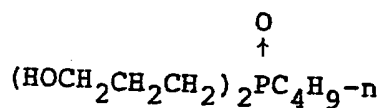
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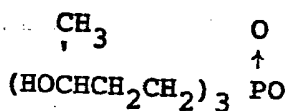
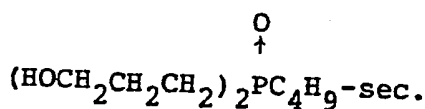
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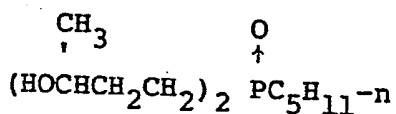
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Polyhydroxyalkylphosphine oxides are a known class of chemical compounds which are described in the technical literature. They may be prepared by first forming the intermediate phosphine by reacting an excess of an olefinic compound with a phosphine compound in the presence of a free radical catalyst. The phosphine adduct is then contacted with an oxidizing agent such as hydrogen peroxide to give the phosphine oxide. Generally speaking, polyhydroxyalkylphosphine oxides are hydrolytically very stable.

The polyurethane adhesive systems aforesaid can be



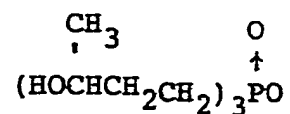
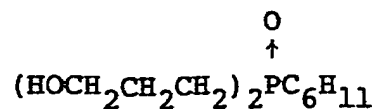
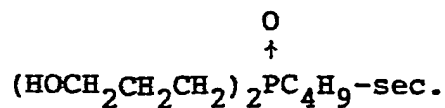
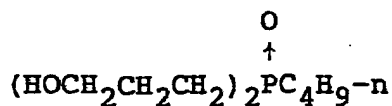
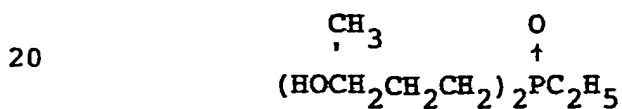
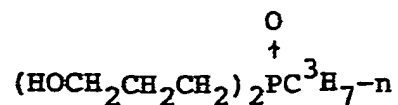
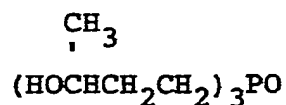
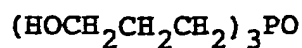
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realized by including as part of the low molecular weight dihydroxy curative, a polyhydroxyalkylphosphine oxide of the formula:

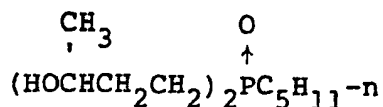


wherein R is alkylene of 3 to 6 carbon atoms,  $R_1$  is an alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 or 3.

Exemplary phosphine oxides within the ambit of the formula aforesaid include:



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In preparing the polyurethane adhesive compositions  
 of the invention, an NCO terminated prepolymer is mixed  
 with a low molecular weight, aliphatic polyhydroxy cura-  
 tive compound in the normal manner of preparing a poly-  
 urethane curable adhesive composition except that there  
 is included therewith a quantity of a polyhydroxyalkyl-  
 phosphine oxide aforesaid and the mixture placed between  
 support plates and allowed to cure. Normally, curing is  
 facilitated by heating at about 200°C. The plates are  
 pressed together during curing; pressure does not usually  
 exceed about 100 lbs/m<sup>2</sup> (45.4Kg/m<sup>2</sup>). After curing for  
 about one hour, the adhesive joint is conditioned at room  
 temperature for about 24 hours.

So far as can be ascertained, the extent of im-  
 proved bonding of the cured adhesive depends on the  
 quantity of polyhydroxyalkylphosphine oxide in the  
 polyurethane curable adhesive formulation. Generally  
 speaking, the polyhydroxyalkylphosphine oxide will run  
 about 10% to about 60% by weight of the total hydroxy  
 curing system. Moreover, the combination of an alipha-  
 tic diol and trihydroxyalkylphosphine oxide has super-  
 ior adhesion compared with the prior art aliphatic  
 diol/triol combination such as the commercial mixture  
 of 1,4-butanediol (BD) and trimethylolpropane (TMP).

The polyurethane curable adhesive compositions of  
 the invention are particularly useful and valuable in  
 that on curing they bond extremely well to aluminum.  
 In some instances, bonding to aluminum was practically  
 the same as on steel. This is unusual and unexpected  
 as good adhesion to aluminum surfaces is recognized in  
 the adhesive art as often being a problem.

It has now been discovered that the enumerated  
 desiderate aforesaid can be realized to a marked degree  
 from heat curable NCO prepolymer/hydroxy curative com-

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position in which at least part of the hydroxy curative is a polyhydroxyalkylphosphine oxide and the provision of said heat curable composition and the heat cured polyurethane coating produced therefrom constitutes the principal object and purpose of the invention. Other objects and purposes will become manifest subsequently.

In carrying out the invention, polyurethane coatings are preferably produced in the known manner of using and formulating ASTM Type III urethanes by applying to a substrate a mixture of a blocked NCO prepolymer and a hydroxy curative containing a trishydroxyalkylphosphine oxide, and the so-treated substrate baked to drive off the blocking agent and promote curing. In the case of phenolic blocked urethane prepolymer, baking is usually effected at temperatures around 350°C.

Blocked urethanes are well-known chemical entities, the description and preparation of which are extensively documented in the patent and technical literature. Generally, an NCO prepolymer is first prepared by reacting excess diisocyanate with a hydrogen donor, for example, polyether or polyester polyol, until maximum reaction is reached as indicated by the desired available NCO percentage after which the blocking agent is introduced to completely block the remaining NCO. To insure complete stability, most formulations include 1 to 2% excess blocking agents. To the blocked prepolymer is then added the equivalent amount of hydrogen donor, for example, amine or polyhydroxy compound to give the heat curable, blocked NCO prepolymer composition. For further details on blocked urethanes and their use in coating formulations, reference is made to the well-known treatise, "The Development and Use of Polyurethane Products" by E. N. Doyle published by McGraw-Hill, Inc. (1971).

Urethane based coatings may be employed using conventional plant procedures such as dipping, electro-

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static spray, corona electric spray, airless spray, flow or curtain coating and other known techniques.

Reference is now made to the following examples and procedures.

5     Examples Of Polyurethane Elastomer Compositions

Example 1

          To 127.5 g of Vibrathane 8011® (a diisocyanate terminated prepolymer of TDI and a polyester polyol; %NCO=3.3, equivalent weight=127.5, sold by Uniroyal), was added 10 g of xylene and the mixture heated to 85°C and degassed. The so-treated prepolymer was then reacted with 10.5 g of a mixture consisting by weight of 15% tris(3-hydroxypropyl) phosphine oxide (THPPO) and 85% sec. butyl bis(3-hydroxypropyl) phosphine oxide (BHPPPO). The mixture was poured onto a metal sheet previously treated with a silicone release agent and then degassed under vacuum. The cast sheet was post cured for 24 hours at 110°C.

Example 2

20     An NCO prepolymer was prepared by adding in portions 2 moles of melted MDI (4,4'-diphenylmethane diisocyanate) to 1 mole of Polymeg 1000, previously degassed and dried overnight at 90°C at 1 mm Hg. Polymeg is a difunctional polyether having an equivalent weight of 502.2 and sold by BASF/Wyandotte. After the addition, the reagents were allowed to react for one hour at no higher temperature than about 80°C. The resulting prepolymer was kept under dry N<sub>2</sub> until ready for use.

30     The prepolymer aforesaid was mixed at room temperature with sec. butyl bis(hydroxypropyl) phosphine oxide at an NCO/OH ratio of 1.05 in the presence of dibutyltin dilaurate as a catalyst. The blended components were poured into a preheated mold at 100°C and held for one hour under 5000 lb. force and then post cured in an oven at 120°C overnight. The resulting elastomer was conditioned in a desiccator for

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one week prior to testing.

Prior Art

MOCA

5 The procedure of Example 1 was repeated using 13 g; (95% of stoichiometric) of MOCA 4,4'-methylene-bis(2-chloroaniline) as the curative.

Prior Art

TMP/BD

10 The procedure of Example 1 was repeated using, as the curative, 4.27 g of a mixture of 6% TMP (trimethylolpropane) and 94% BD (1,4-butanediol).

Elastomer Test Procedures

The polyurethane elastomers of the examples were evaluated using the following standard test procedures:

15 a. Shore hardness - ASTM D-2240-75

Three pieces of elastomer slabs were compiled and the hardness measured by Durometer D.

b. Stress-Strain Properties - ASTM D-412-75

20 The tensile modulus, tensile strength at break and ultimate elongation were measured by Instron Table Model 1130 at room temperature.

The test results of the examples are summarized in Table I.

Examples Of Polyurethane Adhesive Compositions

25 An NCO terminated prepolymer was prepared by adding in portions 2 moles of melted MDI (4,4'-diphenylmethane diisocyanate) to 1 mole of Polymeg 1000, previously degassed and dried overnight at 90°C at 1 mm Hg. Polymeg is a difunctional polyether having an  
30 equivalent weight of 502.2 and sold by BASF. After the addition, the reagents were allowed to react for one hour at no higher temperature than about 80°C. The resulting prepolymer was kept under dry N<sub>2</sub> until ready for use.

35 A curable adhesive composition was prepared by mixing the prepolymer aforesaid with a polyhydroxy-alkylphosphine oxide curative of the invention in the

presence of dibutyltin dilaurate as a catalyst. The thoroughly blended mixture was spread on the surface of 0.5" x 1" degreased metal strips by means of a spatula. Another metal strip was placed with its clean side in contact with the coating. The resulting assembly was inserted in a press, clamped under pressure of not more than about 100 lbs/m<sup>2</sup> (45.4Kg/m<sup>2</sup>) and heated at 200°C for one hour and then allowed to condition at room temperature for 24 hours.

Using the procedure aforesaid, various adhesive formulations of the prepolymers and curative were prepared and tested. These examples and the shear strength data are set forth in Table I.

#### Testing of Adhesives

##### Lap-Shear Strength ASTM-D-3164

a. Testing machine was adjusted in such a way that breaking load for the specimens fell between 15%-85% of full scale.

b. A rate of loading (8.27-9.65 KPa/min.) was applied.

c. Speed of crosshead = 0.05 in/min.

Failing stress was calculated as  $\frac{\text{pounds-force}}{\text{in}^2 \text{ -area}}$

Turning to Table II, it will be observed that where 1,4-butanediol (BD) is used in combination with BHPPO alone or with THPPO, Examples 4, 5, 6, 9 and 10, excellent adhesion to steel and aluminum was achieved. With higher amounts of BHPPO, adhesion increased; Examples 4, 5 and 6. Improved adhesion likewise resulted with increased amounts of THPPO. The best adhesion resulted when both BHPPO and THPPO were both used in the curative system.

Example 10 is particularly noteworthy in that the adhesion to aluminum was excellent, virtually as good as to steel.

Example 11, the THPPO triol of the invention was replaced with the prior art control TMP triol. The

adhesion to aluminum dropped to 2011.0 kPa compared with 3734.2 kPa of Example 9 containing THPPO triol.

The prior art with BD and TMP compositions a. and b. give much lower shear strengths than were obtained with the polyhydroxyalkylphosphine oxide curatives of the invention.

#### Examples Of Polyurethane Coating Compositions

	<u>Identi-</u> <u>fication</u>	<u>Chemical</u> <u>Composition</u>	<u>Mol.</u> <u>Wt.</u>	<u>Eq.</u> <u>Wt.</u>	<u>Sup-</u> <u>plier</u>
10	<u>Hydroxyl</u> <u>Components</u>				
	THPPO	Tris(3-hydroxypropyl) phosphine oxide	224.0	74.66	FMC Corp.
15	Desmophen 650	Hydroxy terminated polyester resin		215.00	Mobay Chem.
20	Crelan U-502	Hydroxy terminated polyester resin		1133.30	Mobay Chem.
25	Epoxy Resin Epon 1001	Epoxy-hydroxy terminated resin	1000.0	500.00	Shell
30	Trimethylol propane	Trifunctional hydroxyl compound	134.0	44.60	
	<u>Isocyanate</u> <u>Components</u>				
35	Crelan Hardener U-T m.temp. 60°C	Blocked aromatic diisocyanate adduct	672.0	336.0	Mobay Chem.

Crelan Hard-	Blocked ali-	730.4	365.2	Mobay
ener U-I	phatic diiso-			Chem.
	cyanate adduct			

Other5 Components

Catalyst T-12	Dibutyltin dilaurate	M & T
(DBTDL)		Chem.
		Inc.

10	Modaflow-	
	flow agent	Mon-
		santo

	Silicone	
	fluid L-	Union
15	522-flow agent	Car-
		bide

MEK Solvent	Methylethylketone
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The examples of the invention and the prior art were formulated using one of the following mixing procedures.

20 Mixing Procedures

A. Dibutyltin dilaurate (DBTDL) catalyst is dissolved in methylethylketone (MEK) and the solution sprayed over a pulverized blend of the NCO and OH components. The solvent is removed after which the solidified residue is ground in a ball mill for 24 hours. A solids fraction passing through a 150 mesh sieve was collected and the powder sprayed on grounded metal panels with an electrostatic spray gun and the resulting layer baked at 200°C.

30 B. The OH components, DBTDL catalyst and flow agent are mixed and melted to give a homogeneous blend. After solidifying, the blend is crushed and mixed with the NCO component. The solids are transferred to a ball mill and ground for 24 hours. A fraction passing 35 a 150 mesh sieve was sprayed with an electrostatic spray gun on grounded metal panels which were baked at 200°C.



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C. The catalyst (DBTDL), flow agent, pulverized NCO and OH components are melted together at 90°C and mixed until a homogeneous blend is obtained. On cooling to room temperature, the solidified mass is crushed and ground in a ball mill for 48 hours. A portion passing through a 150 mesh sieve is collected. This fraction is sprayed on grounded metal panels with an electrostatic spray gun and baked at 200°C.

D. Dibutyltin dilaurate (DBTDL) catalyst, OH and NCO components and modaflow-flow agent are mixed at room temperature in a blender for 2 minutes. The solids are then crushed and ground in a glass bowl by hand for 10 to 20 minutes. The ground powders are sifted through a 150 mesh sieve and the sifted portion sprayed on grounded metal panels with an electrostatic spray gun and the resulting coating baked at 200°C.

#### Coating Test Procedures

1. Appearance of powder is observed visually determining smoothness of flow, orange peel on the surface, etc.
2. Mar-proofness is determined by just scraping under pressure with a reverse nail over the surface of the film. If no residual scraping mark was left, the film is considered to be mar-proof.
3. Discoloration after baking is determined visually.
4. Solvent Resistance, ASTM D 2792-60. Small cotton balls are placed on the coated panel and were soaked with a solvent. The films are checked every hour for softening, swelling, blistering and solubility.
5. Impact Strength. Impact test is run on Bonderite 37 steel panels according to ASTM D 2794-69. A Gardner impact test is used containing a 4 lb. steel rod, 1/2" diameter male punch and 9/16" diameter die.
6. Sward Hardness. The Sward hardness is measured with a Sward rocker on glass panels, according to

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ASTM D 1684.

Example 11\*

	Equiva-		Equiv. %
	lents of	Parts by	in
	<u>NCO or OH</u>	<u>Weight</u>	<u>OH Comp.</u>
5 <u>NCO Component</u>			
Aromatic blocked	1.05	100.0	
diisocyanate,			
Crelan Hardener U-T			
<u>Hydroxyl Component</u>			
10 THPPO	0.64	14.0	64.0
Desmophen 650	0.23	14.0	23.0
Epoxy Resin 1001	0.13	21.5	<u>13.0</u>
			100.00
<u>Other Additives</u>			
15 T-12, catalyst DBTDL		00.7	
Modaflow-flow agent		2.0	
MEK		40.0	

Curing Conditions

Baking Temp. &amp; Time: 200°C, 6 min.

Testing Results

- 20 1. Appearance of Film: a. Flow: good  
b. Mar-proofness: good
2. Discoloration After Baking: yellowing
3. Solvent Resistance: a. Toluene: no effect  
b. Isopropanol: no effect
- 25 4. Impact Strength: a. Direct: Joule In./lb.  
5.2 46  
b. Reverse: 2.9 26
5. Sward Hardness: 44

\*Mixing procedure A was followed

30 Example 12\*

	Equiva-		Equiv. %
	lents of	Parts by	in
	<u>NCO or OH</u>	<u>Weight</u>	<u>OH Comp.</u>
<u>NCO Component</u>			
Aliphatic blocked	1.05	100.00	
35 diisocyanate, Cre-			
lan Hardener U-I			

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Hydroxyl Components

THPPO	0.64	12.83	64.0
Desmophen 650	0.23	12.83	23.0
Epoxy Resin 1001	0.13	17.12	<u>13.0</u>
5			100.0

Other Additives

T-12, catalyst DBTDL	0.75
Modaflow-flow agent	2.00
MEK	40.00

10 Curing Conditions

Baking Temp. &amp; Time: 200°C, 10 min.

Testing Results

1. Appearance of Film:
  - a. Flow: good
  - b. Mar-proofness: good
- 15 2. Discoloration After Baking: Does not discolor
3. Solvent Resistance:
  - a. Toluene: no effect
  - b. Isopropanol: no effect
  - c. Ethyl Acetate: no effect
- 20 4. Impact Strength:
 

	<u>Joule</u>	<u>In./lb.</u>
a. Direct:	8.6	76
b. Reverse:	5.2	46

5. Sward Hardness: 42

\*Mixing procedure A was followed

Example 13\*

25	Equiva-		Equiv. %
	lents of	Parts by	in
		Weight	
<u>NCO Component</u>	<u>NCO or OH</u>		<u>OH Comp.</u>
Aliphatic blocked	1.05	100.0	
diisocyanate, Crelan			
30 Hardener U-I			
<u>Hydroxyl Component</u>			
THPPO	0.70	14.0	70.0
Desmophen 650	0.25	14.0	25.0
Epoxy Resin 1001	0.05	7.0	<u>5.0</u>
35			100.0

Other Additives

T-12, catalyst DBTDL	0.5
----------------------	-----

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Modaflow-flow agent 1.50

Curing Conditions

Baking Temp. &amp; Time: 200°C, 15 min.

Testing Results

- 5 1. Appearance of Film: a. Flow: good  
b. Mar-proofness: good
2. Discoloration After Baking: Does not discolor
3. Solvent Resistance: a. Toluene: no effect  
b. Isopropanol: no effect  
10 c. Ethyl Acetate: no effect
- |    |                             | <u>Joule</u> | <u>In./lb.</u> |
|----|-----------------------------|--------------|----------------|
| 4. | Impact Strength: a. Direct: | 6.8          | 60             |
|    | b. Reverse:                 | 3.4          | 30             |
| 5. | Sward Hardness:             | 50           |                |

15 \*Mixing Procedure B was followed

Example 14\*

	Equiva-		Equiv. %
	lents of	Parts by	in
<u>NCO Component</u>	<u>NCO or OH</u>	<u>Weight</u>	<u>OH Comp.</u>
20 Aliphatic blocked diisocyanate, Cre-	1.050	100.00	
lan Hardener U-I			
<u>Hydroxyl Component</u>			
THPPO	.775	17.03	77.5
25 Desmophen 650	.175	10.22	17.5
Epoxy Resin 1001	.050	6.81	<u>5.0</u>
			100.0

Other Additives

- T-12, catalyst 0.50
- 30 Modaflow-flow agent 2.00

Curing Conditions

Baking Temp. &amp; Time: 200°C, 10 min.

Testing Results

- 35 1. Appearance of Film: a. Flow: good  
b. Mar-proofness: good
2. Solvent Resistance: a. Toluene: no effect  
b. Isopropanol: no effect



No No No No No No Soft  
Effect

5	Ethyl Acetate	Soft	Blis- tering
---	------------------	------	-----------------

In the following Examples 16-17, mixing procedure D was followed.

### Example 16

	Equivalent of NCO or OH	Parts by Weight
10 <u>NCO Component</u>		
Aliphatic blocked	1.05	50.00
diisocyanate Crelan		
Hardener, U-I		
<u>Hydroxyl Component</u>		
15 THPPO	0.7500	7.81
Creilan U-502	0.1875	27.70
Epoxy Resin 1001	0.0625	4.07
<u>Other Additives</u>		
T-12, catalyst DBTDL		0.375
20 Modaflow-flow agent		1.000
		(2.5%)

### Curing Conditions

Baking Temp. and Time: 200°C, 10 min.

### Testing Results

- 25 1. Appearance of Film: a. Flow: good  
b. Mar-proofness: good  
2. Discoloration After Baking: Does not discolor

		<u>Joule</u>	<u>In./lb.</u>
30	3. Impact Strength: a. Direct:	13.6	120
	b. Reverse:	5.6	50

4. Sward Hardness: 38  
5. Solvent Resistance:

Time

	<u>Solvent</u>	<u>(Hr.)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
35	Toluene		No	No	Soft	S	S	S	S
		Effect							

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	Isopropanol	No	No	No	No	No	No	No	
	Ethyl Acetate	Soft Blis- tering							
5		<u>Example 17</u>							
		Equivalents of					Parts by		
	<u>NCO Components</u>	<u>NCO or OH</u>					<u>Weight</u>		
	Aliphatic blocked	1.05					30.00		
	diisocyanate, Crelan								
10	Hardener, U-I								
	<u>Hydroxyl Component</u>								
	THPPO	1.00					6.01		
	<u>Other Additives</u>								
15	T-12, catalyst DBTDL						0.225		
	Modaflow-flow agent						0.60		
							(10.0%)		
	<u>Curing Conditions</u>								
	Baking Temp. and Time:	200°C, 10 min.							
20	<u>Testing Results</u>								
	1. Appearance of Film:	a. Flow: good							
		b. Mar-proofness: good							
	2. Discoloration After Baking:	Does not discolor							
							<u>Joule</u>	<u>In./lb.</u>	
25	3. Impact Strength:	a. Direct:	5.6			50			
		b. Reverse:	1.7			15			
	4. Sward Hardness:	36							
	5. Solvent Resistance:								
		Time							
30	<u>Solvent</u>	<u>(Hr.)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
	Toluene		No	No	No	Soft	S	S	S
	Isopropanol		No	No	No	Soft	S	S	S
35	Ethyl Acetate		Soft	S	S	S	S	S	S

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		<u>Prior Art (a)</u>							
		Equivalent of		Parts by					
		<u>NCO or OH</u>		<u>Weight</u>					
5	<u>NCO Component</u>								
	Aliphatic blocked	1.05		20.00					
	diisocyanate, Crelan								
	Hardener, U-I								
	Creilan U-502	0.80		47.28					
	Epoxy Resin 1001	0.20		5.22					
10	<u>Other Additives</u>								
	T-12, catalyst DBTDL			0.15					
	Modaflow-flow agent			0.40					
				(0.8%)					
	<u>Curing Conditions</u>								
15	Baking Temp. and Time: 200°C, 12 min.								
	<u>Testing Results:</u>								
	1. Appearance of Film: a. Flow: good								
	b. Mar-proofness: good								
	2. Discoloration After Baking: Does not discolor								
20		<u>Joule</u>		<u>In./lb.</u>					
	3. Impact Strength: a. Direct:	18.1		160					
	b. Reverse:	18.1		160					
	4. Sward Hardness: 38								
	5. Solvent Resistance:								
25	Time								
	<u>Solvent</u>	<u>(Hr.)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
	Toluene	No	Soft	S	S	S	S	S	S
		Effect							
30	Isopropanol	No	No	No	No	No	No	No	No
	Ethyl Acetate	Soft	Blis-						
			tering						



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Prior Art (b)

<u>NCO Component</u>		<u>Equivalents of</u> <u>NCO or OH</u>	<u>Parts by</u> <u>Weight</u>
5	Aliphatic blocked diisocyanate, Crelan Hardener, U-I	1.05	50.000
<u>Hydroxyl Component</u>			
	Trimethylolpropane,	0.80	4.653
	TMP Crelan, U-502	0.20	29.554
10	<u>Other Additives</u>		
	T-12, catalyst DBTDL		0.375
	Modaflow-flow agent		0.630
			(1.8%)
<u>Curing Conditions</u>			
15	Baking Temp. and Time: 200°C, 12 min.		
<u>Testing Results</u>			
	1. Appearance of Film: a. Flow: good		
	b. Mar-proofness: good		
	2. Discoloration After Baking: Does not discolor		
20		<u>Joule</u>	<u>In./lb.</u>
	3. Impact Strength: a. Direct:	9.0	80
	b. Reverse:	5.6	50
	4. Sward Hardness: 38		
	5. Solvent Resistance:		
25	<u>Solvent</u>	<u>Time</u> <u>(Hr.)</u>	
		<u>1</u>	<u>2</u> <u>3</u>
	Toluene	Soft	Dissolving D
	Isopropanol	Soft	Dissolving D
30	Ethyl Acetate	Soft	Dissolving D

TABLE IElastomer Properties

<u>Example</u>	<u>Hardness</u> <u>Shore A</u>	<u>Tensile</u> <u>MPa</u>	<u>Elongation</u> <u>-%</u>	<u>Modulus</u> <u>kPa</u>
1	50	17.24 <sup>b</sup>	700	-----
2	33	3.33	640.63	806.4 (100%) 1108.8 (200%) 1411.2 (300%)

PRIOR ART

MOCA	80	6260	393	-----
TMP/BD 6%/94%	48	523 <sup>a</sup>	714	-----

<sup>a</sup> Jaw break<sup>b</sup> Sample pulled out of jaws

TABLE II

<u>Example</u>	<u>Formulation</u>	<u>Steel</u> <u>Strip</u>	<u>Aluminum</u> <u>Strip</u>
3	(1,4BD, eq. wt. 80% + BHPPO by eq. wt. 20%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.25	0.25
	BHPPO, g	0.06	0.06
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	4309.2	3519.1
4	(1,4BD by eq. wt. 60% + BHPPO by eq. wt. 40%)		
	polyurethane, prepolymer, g	5.00	5.00
	1,4BD, g	0.22	0.22
	BHPPO, g	0.15	0.15
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	4757.4	4550.5
5	(1,4BD by eq. wt. 40% + BHPPO by eq. wt. 60%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.17	0.17
	BHPPO, g	0.26	0.26
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	5458.3	5171.1
6	(1,4BD by eq. wt. 90% + THPPO by eq. wt. 10%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.26	0.26
	BHPPO, g	0.03	0.03
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	3171.6	1578.9

TABLE II (continued)

<u>Example</u>	<u>Formulation</u>	<u>Steel</u>	<u>Aluminum</u>
		<u>Strip</u>	<u>Strip</u>
7	(1,4BD by eq. wt. 80% + THPPO by eq. wt. 20%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.24	0.24
	THPPO, g	0.06	0.06
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	4688.4	4274.7
8	(1,4BD by eq. wt. 70% + BHPPO by eq. wt. 20% + THPPO by eq. wt. 10%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.22	0.22
	BHPPO, g	0.06	0.06
	THPPO, g	0.03	0.03
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	5108.9	3734.6
9	(1,4BD by eq. wt. 60% + BHPPO by eq. wt. 20% + THPPO by eq. wt. 20%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.20	0.20
	BHPPO, g	0.07	0.07
	THPPO, g	0.07	0.07
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	5309.9	5102.1

TABLE II (continued)

<u>Example</u>	<u>Formulation</u>	<u>Steel Strip</u>	<u>Aluminum Strip</u>
10	(1,4BD by eq. wt. 70% + BHPPO by eq. wt. 20% + TMP by eq. wt. 10%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.21	0.21
	BHPPO, g	0.06	0.06
	TMP, g	0.03	0.03
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	3874.8	2011.2

PRIOR ART

a	(1,4BD, eq. wt. 100%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.27	0.27
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	3016.5	2011.2
b	(1,4BD by eq. wt. 90% + TMP by eq. wt. 10%)		
	polyurethane prepolymer, g	5.00	5.00
	1,4BD, g	0.24	0.24
	TMP, g	0.03	0.03
	NCO/OH	1.10	1.10
	Lap Shear, strength, kPa	2011.0	1436.5

BD = 1,4-butanediol

TMP = trimethylolpropane

THPPO = tris(3-hydroxypropyl) phosphine oxide

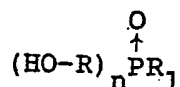
BHPPO = sec. butyl bis(3-hydroxypropyl) phosphine oxide

## CLAIMS:

1. Polyurethane compositions consisting of:

A. A polyurethane elastomer product of an NCO terminated elastomer prepolymer formed from a polyol selected from the class consisting of polyhydroxy functional polyethers and polyesters cured with a curative containing a polyhydroxyalkyl phosphine oxide curative of the formula:

5



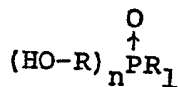
10

wherein R is alkylene of 3 to 6 carbon atoms, R<sub>1</sub> is alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 to 3,

15

B. A curable polyurethane composition comprising an NCO terminated urethane prepolymer from a polyol selected from the class consisting of polyhydroxy functional polyethers and polyesters and a polyhydroxy aliphatic curative system, the improvement of incorporating in the curative system from about 10% to about 60% based on the weight of the curative system of a polyhydroxyalkylphosphine oxide of the formula:

20



25

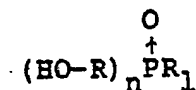
wherein R is alkylene of 3 to 6 carbon atoms, R<sub>1</sub> is alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 to 3, and

30

C. A heat curable polyurethane coating composition comprising a blocked urethane NCO prepolymer and a hydroxy curative at least part of which is a polyhydroxyalkylphosphine oxide of the formula:

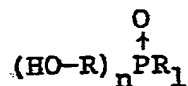
35

-30-



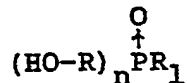
wherein R is alkylene of 3 to 6 carbon atoms,  
 $\text{R}_1$  is an alkyl of 2 to 10 carbon atoms,  
 cycloalkyl of 6 to 12 carbon atoms and n is  
 an integer to 2 or 3.

2. A polyurethane elastomer product of an NCO terminated elastomer prepolymer formed from a polyol selected from the class consisting of polyhydroxy functional polyethers and polyesters cured with a curative containing a polyhydroxyalkyl phosphine oxide curative of the formula:



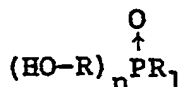
wherein R is alkylene of 3 to 6 carbon atoms,  $\text{R}_1$  is alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 to 3.

3. A curable polyurethane composition comprising an NCO terminated urethane prepolymer from a polyol selected from the class consisting of polyhydroxy functional polyethers and polyesters and a polyhydroxy aliphatic curative system, the improvement of incorporating in the curative system from about 10% to about 60% based on the weight of the curative system of a polyhydroxyalkylphosphine oxide of the formula:



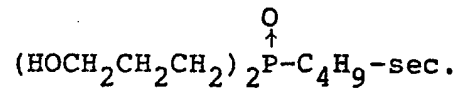
wherein R is alkylene of 3 to 6 carbon atoms,  $\text{R}_1$  is alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 to 3.

4. A heat curable polyurethane coating composition comprising a blocked urethane NCO prepolymer and a hydroxy curative at least part of which is a polyhydroxyalkylphosphine oxide of the formula:

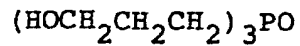


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16. The composition of claim 4 wherein the phosphine oxide is:



17. The composition of claim 4 wherein the phosphine oxide is:



18. A cured polyurethane adhesive from the curable composition of claim 4.

19. The cured polyurethane adhesive from the curable composition of claim 19.

20. The cured polyurethane adhesive from the curable composition of claim 20.

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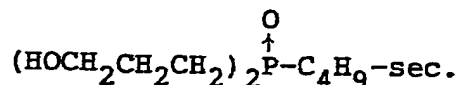
-31-

wherein R is alkylene of 3 to 6 carbon atoms,  $R_1$  is an alkyl of 2 to 10 carbon atoms, cycloalkyl of 6 to 12 carbon atoms and n is an integer of 2 or 3.

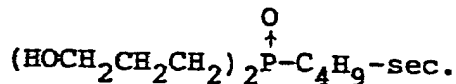
5        5.    The elastomer product of claim 2 wherein the NCO terminated prepolymer is formed by reacting the polyol with toluene diisocyanate.

6.    The elastomer product of claim 2 wherein the NCO terminated prepolymer is formed by reacting the polyol with 4,4'-diphenylmethanediisocyanate.

10       7.    The elastomer product of claim 2 wherein the curative is the compound:



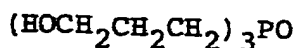
15       8.    The elastomer product of claim 2 wherein the curative is a mixture of a major amount of:



and a minor amount of:



9.    The elastomer of claim 2 wherein the curative is the compound:



25       10.   The composition of claim 3 wherein a portion of the hydroxyl curative is a polyhydroxyalkylphosphine oxide.

11.   The composition of claim 3 wherein the sole hydroxyl curative is a polyhydroxyalkylphosphine oxide.

30       12.   The composition of claim 12 wherein the polyhydroxyalkylphosphine oxide is tris(3-hydroxypropyl) phosphine oxide.

13.   A coating produced by heat curing the coating composition of claim 3.

35       14.   A coating produced by heat curing the coating composition of claim 12.

15.   A coating produced by heat curing the coating composition of claim 13.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0122894  
Application number

EP 84 85 0085

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 2)
A	US-A-3 268 360 (J.V. BENINATE et al.)		C 08 G 18/10 C 08 G 18/38 C 09 D 3/72 C 09 J 3/16
A	--- CHEMICAL ABSTRACTS, vol. 78, no. 18, 7th May 1973, page 53, no. 112481z, Columbus, Ohio, US; R.K. VALETDINOV et al.: "Properties of phosphorus-containing polyether urethane elastomers" & KAUCH. REZINA 1972, 31(11), 15-17 -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 2)
			C 08 G C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-06-1984	Examiner VAN PUymbroeck M.A.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	